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(54) **PHOSPHOR MATERIALS AND RELATED DEVICES**

(71) Applicant: **GENERAL ELECTRIC COMPANY**, Schenectady, NY (US)

(72) Inventors: **Prasanth Kumar Nammalwar**, Karnataka (IN); **Digamber Gurudas Porob**, Karnataka (IN); **Anant Achyut Setlur**, Niskayuna, NY (US); **Satya Kishore Manepalli**, Karnataka (IN)

(73) Assignee: **GENERAL ELECTRIC COMPANY**, Schenectady, NY (US)

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C09K 11/64	(2006.01)
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H01J 61/44	(2006.01)
C07D 301/19	(2006.01)
C09K 11/77	(2006.01)
C07C 1/24	(2006.01)
C07C 5/03	(2006.01)
C07C 29/132	(2006.01)
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See application file for complete search history.

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Primary Examiner — Carol M Koslow

(74) *Attorney, Agent, or Firm* — GE Global Patent Operation; Peter T. DiMauro

(57) **ABSTRACT**

A phosphor material is presented that includes a blend of a first phosphor, a second phosphor and a third phosphor. The first phosphor includes a composition having a general formula of $RE_{2-y}M_{1+y}A_{2-y}Sc_ySi_{n-w}Ge_wO_{12+\delta}:Ce^{3+}$ wherein RE is selected from a lanthanide ion or Y^{3+}, where M is selected from Mg, Ca, Sr or Ba, A is selected from Mg or Zn and where $0 \le y \le 2$, $2.5 \le n \le 3.5$, $0 \le w \le 1$, and $-1.5 \le \delta \le 1.5$. The second phosphor includes a complex fluoride doped with manganese (Mn^{4+}), and the third phosphor include a phosphor composition having an emission peak in a range from about 520 nanometers to about 680 nanometers. A lighting apparatus including such a phosphor material is also presented. The light apparatus includes a light source in addition to the phosphor material.

8 Claims, 4 Drawing Sheets

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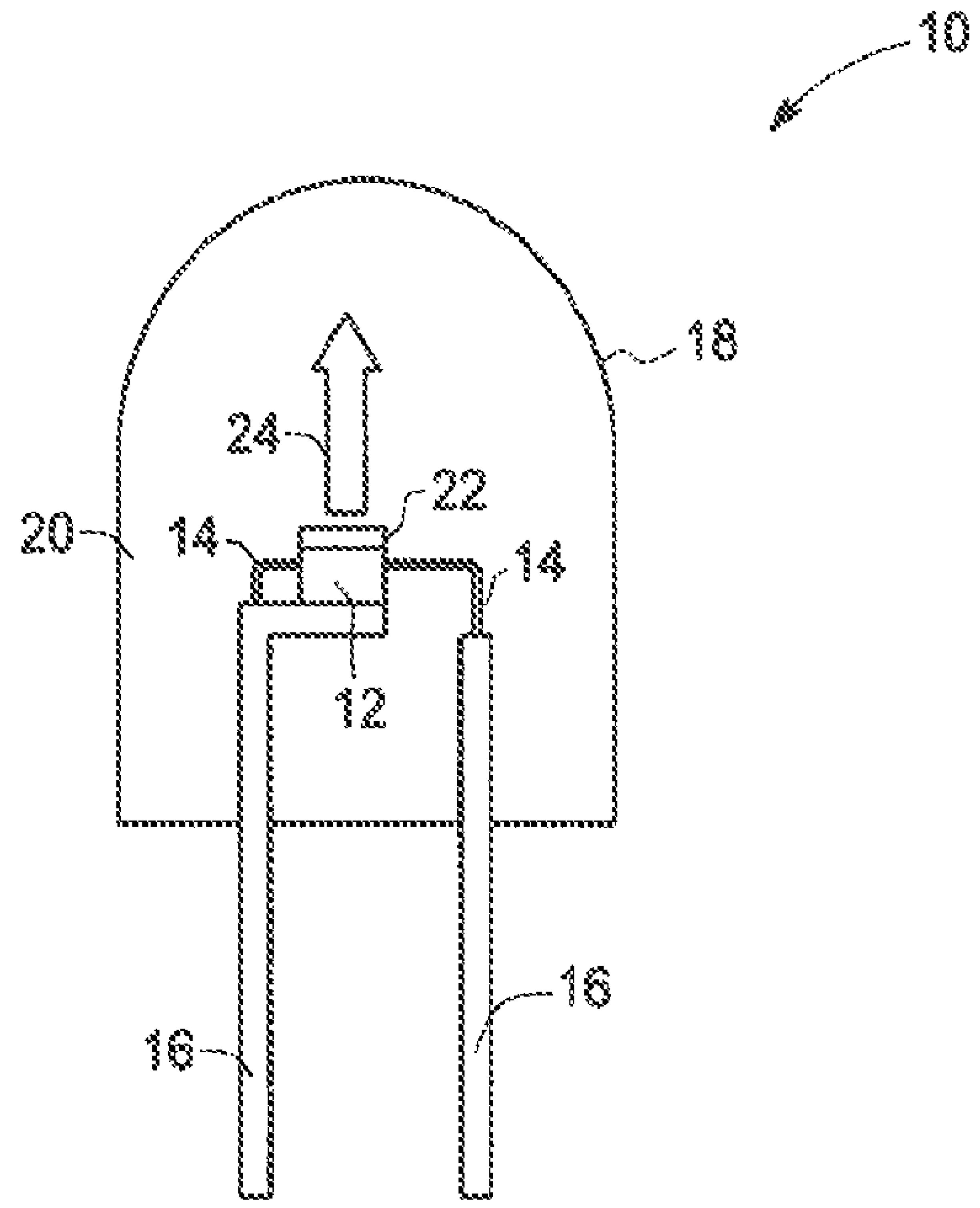


FIG. 1

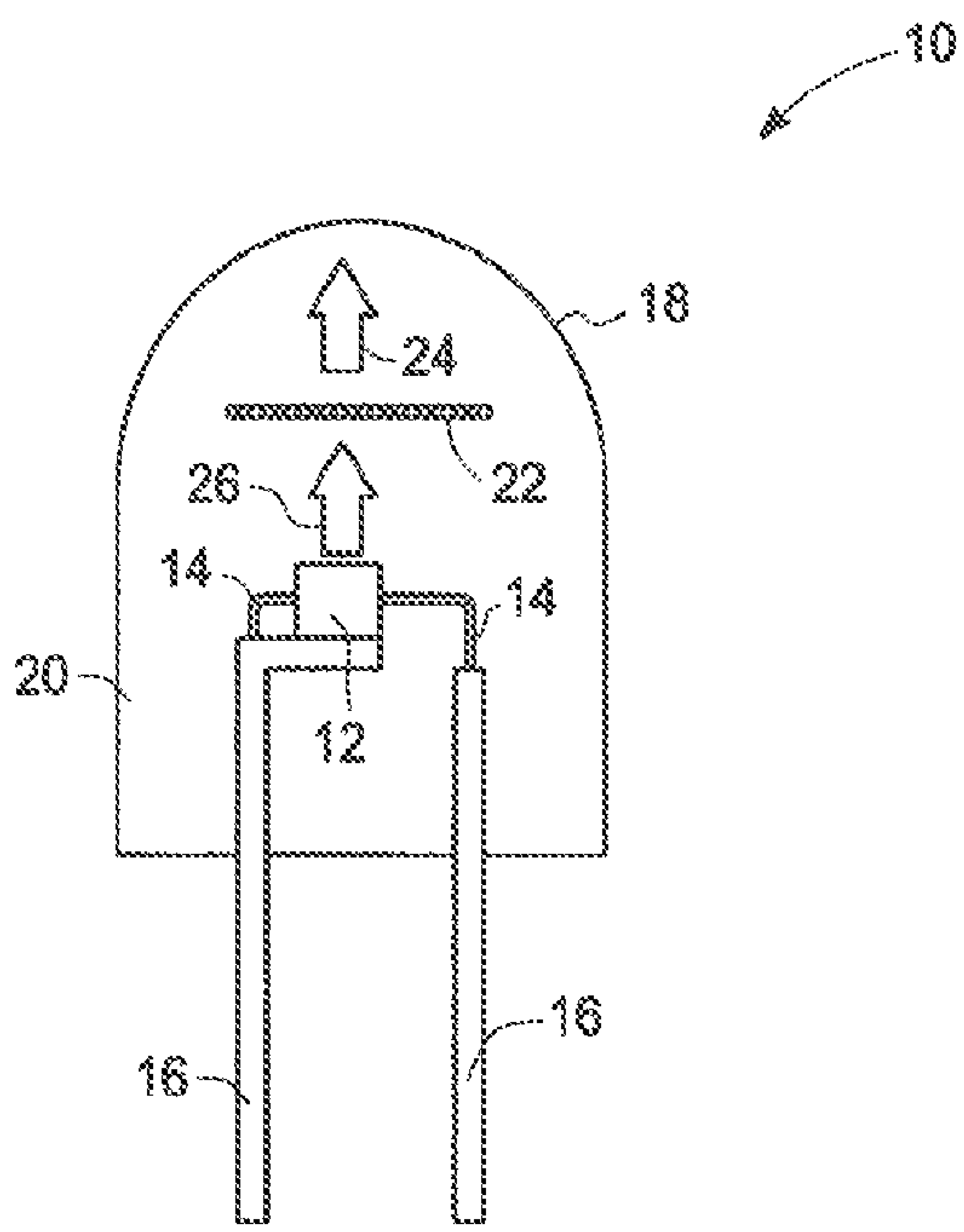


FIG. 2

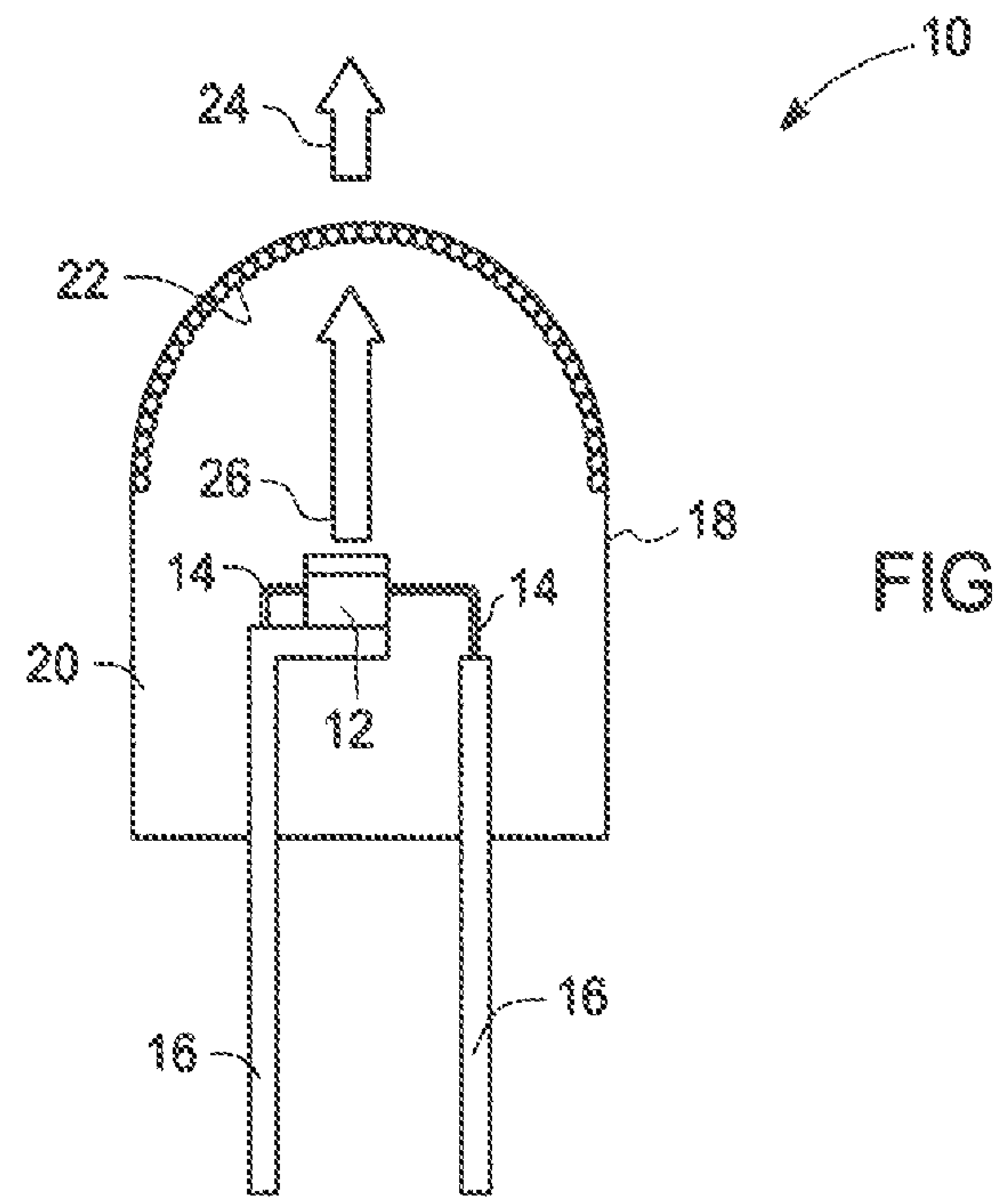


FIG. 3

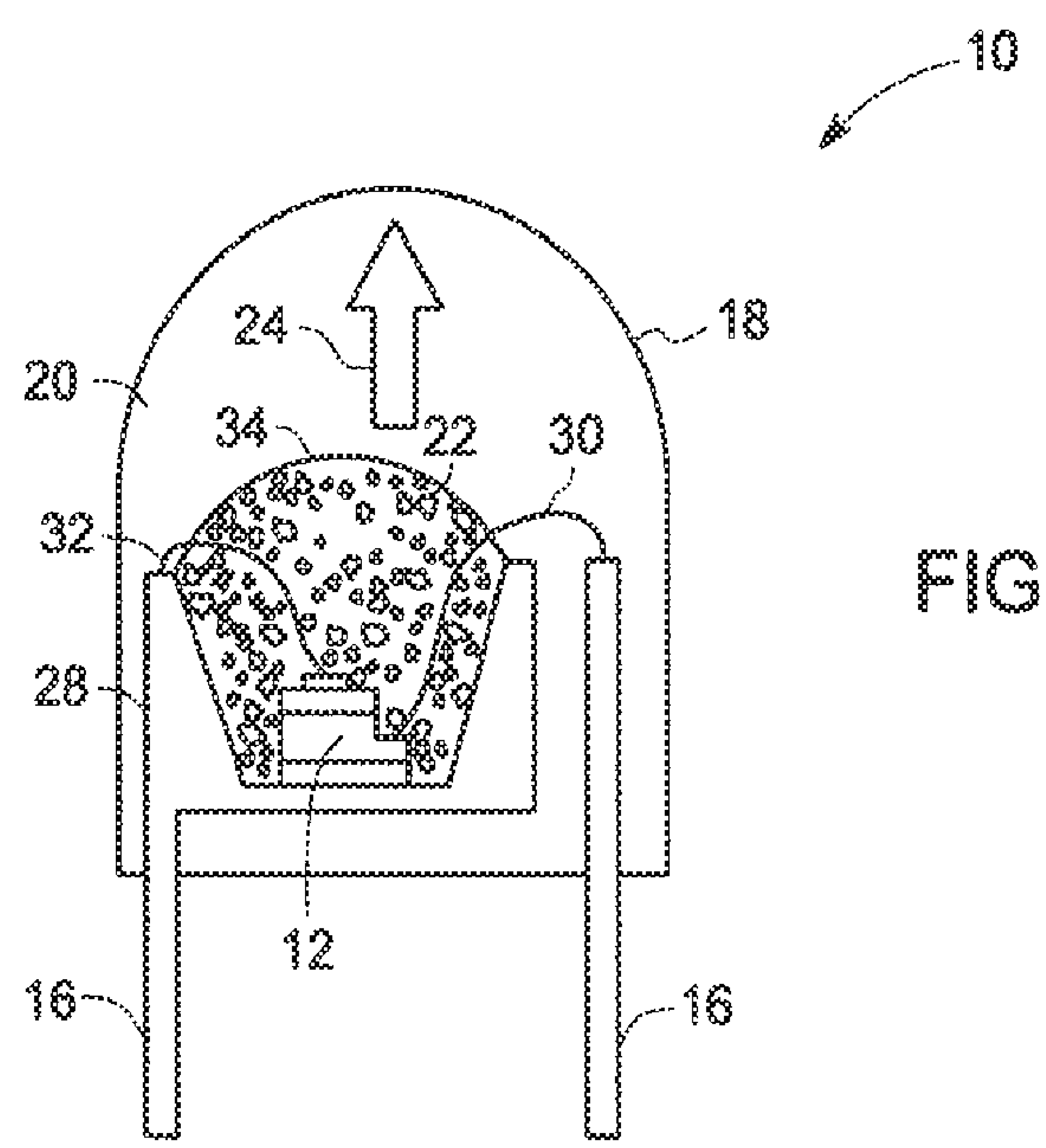
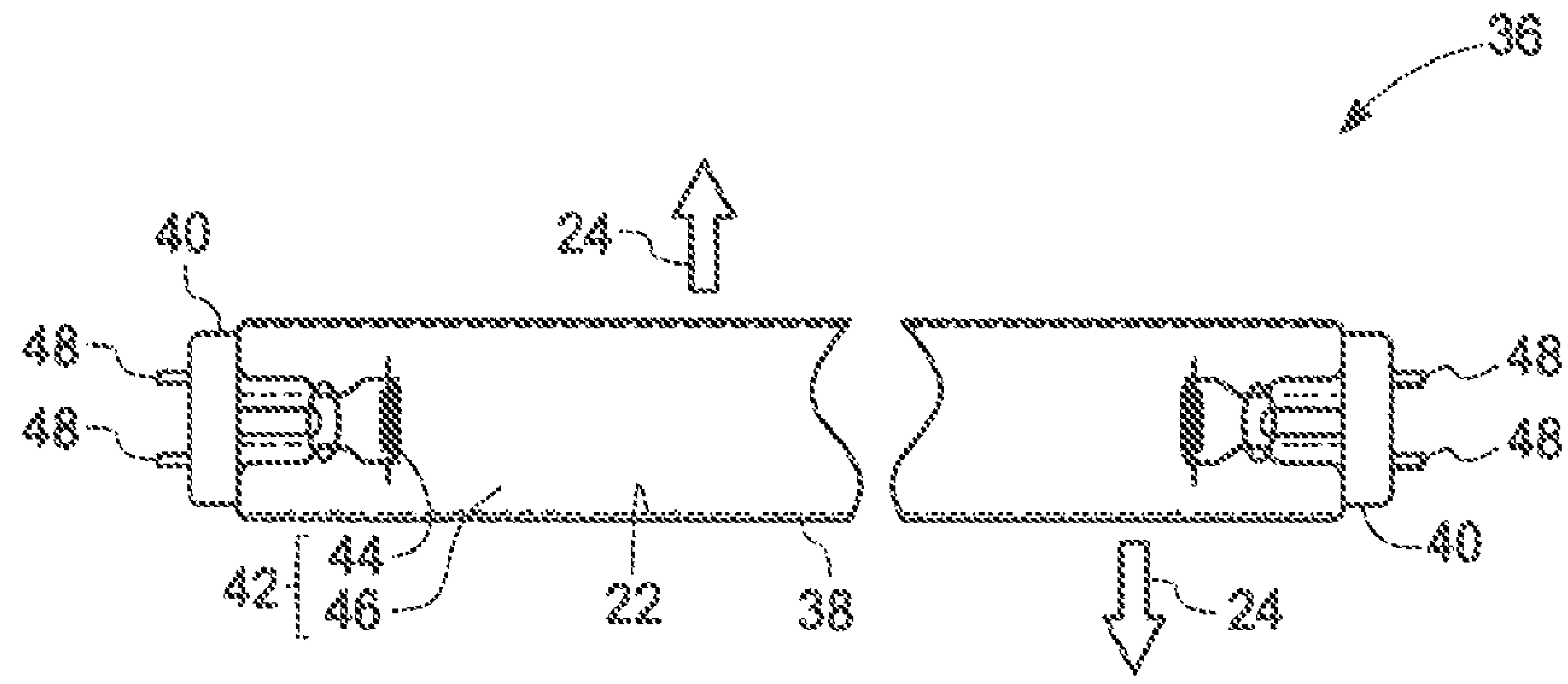


FIG. 4


36
24
40
48
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48
48
44
42
46
22
38
40
24

FIG. 5

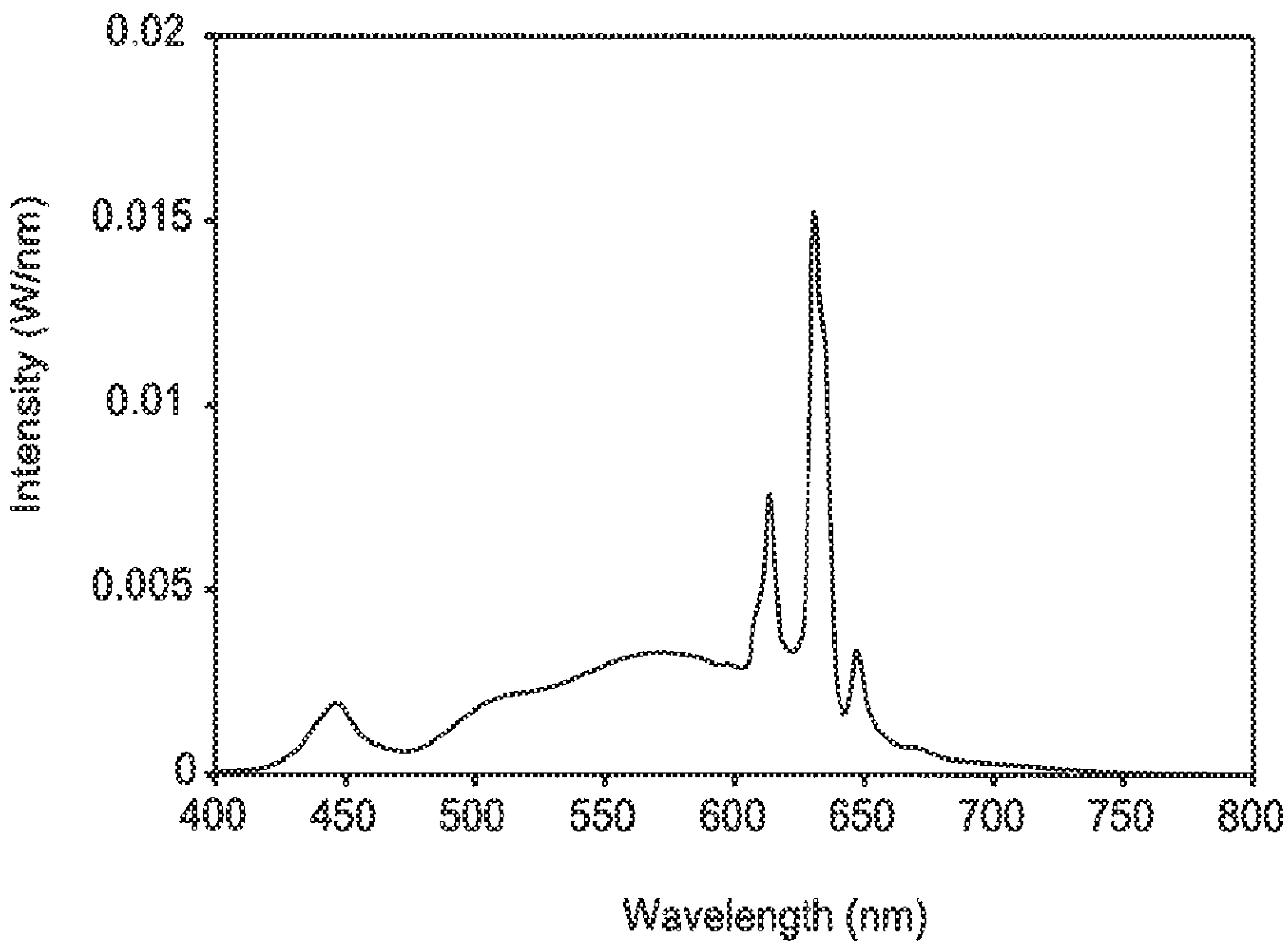
0.02
0.015
0.01
0.005
0
Intensity (W/nm)
400
450
500
550
600
650
700
750
800
Wavelength (nm)

FIG. 6

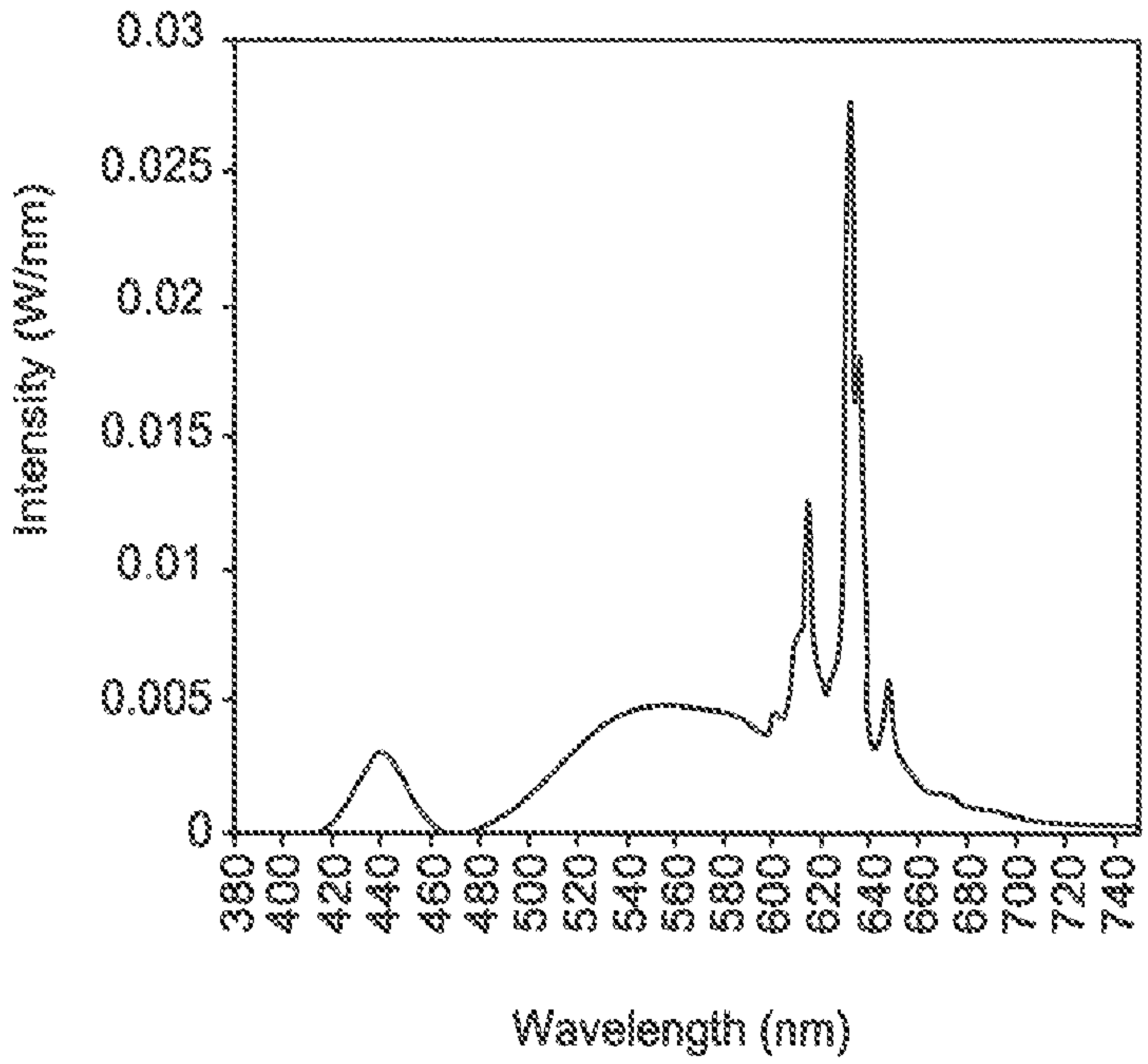
0.03
0.025
0.02
0.015
0.01
0.005
0
Intensity (W/nm)
380
400
420
440
460
480
500
520
540
560
580
600
620
640
660
680
700
720
740
Wavelength (nm)

FIG. 7

PHOSPHOR MATERIALS AND RELATED DEVICES

BACKGROUND

The invention relates generally to phosphor blends for wavelength conversion, and specifically phosphor blends for the conversion of radiation emitted by a light source. More particularly, the invention relates to phosphor blends for use with the blue light emitting diodes (LEDs).

A phosphor is a luminescent material that absorbs radiation energy in a portion of the electromagnetic spectrum and emits radiation energy in another portion of the electromagnetic spectrum. One important class of phosphors includes crystalline inorganic compounds of very high chemical purity and of controlled composition to which small quantities of other elements (called "activators") have been added to convert them into efficient fluorescent materials. With the right combination of activators and inorganic compounds, the color of the emission can be controlled. Most useful and well-known phosphors emit radiation (also referred to as light herein) in the visible portion of the electromagnetic spectrum in response to excitation by electromagnetic radiation outside the visible range. For example, the phosphors have been used in mercury vapor discharge lamps to convert the ultra-violet (UV) radiation emitted by the excited mercury to visible radiation. Further, the phosphors may be used in a light emitting diode (LED) to generate colored emissions that may generally not be obtained from the LED itself.

Light emitting diodes (LEDs) are semiconductor light emitters often used as a replacement for other light sources, such as incandescent lamps. They are particularly useful as display lights, warning lights and indicating lights or in other applications where a colored light is desired. The color of light produced by an LED is dependent on the type of the semiconductor material used in its manufacture. The colored LEDs are often used in toys, indicator lights and other devices.

The colored semiconductor light emitting devices, including light emitting diodes and lasers (both are generally referred to as LEDs herein), have been produced from Group III-V alloys such as gallium nitride (GaN). With reference to the GaN-based LEDs, light is generally emitted in the UV and/or blue range of the electromagnetic spectrum. Until quite recently, the LEDs have not been suitable for lighting uses where a bright white light is needed, due to the inherent color of the light produced by the LEDs.

Techniques have been developed for converting the light emitted from the LEDs to useful light for illumination purposes. In one technique, the LED is coated or covered with a phosphor layer. The phosphor absorbs radiation generated by the LED, and generates radiation of a different wavelength, for example, in the visible range of the spectrum.

A combination of LED generated light and phosphor generated light may be used to produce white light. The most popular white LEDs are based on blue emitting GaInN chips. The blue emitting LEDs are coated with a phosphor or a phosphor blend including red, green and blue emitting phosphors that converts some of the blue radiation to a complementary color, for example a yellow-green emission. The total of the light from the phosphor and the LED chip provides white light having a color point with corresponding color coordinates (x and y) and correlated color temperature (CCT), and its spectral distribution provides a color rendering capability, measured by the color rendering index (CRI).

These white LEDs typically produces white light with a CRI between about 70 and about 80 for a tunable CCT greater than about 4000K. While such white LEDs are suitable for some applications, it is desirable to produce white light with higher CRIs (greater than about 90) and lower CCT (less than 3000K) for many other applications.

Therefore, it would be desirable to provide new and improved phosphor blends that produce white light with high CRI and high lumen for low CCT.

BRIEF DESCRIPTION

Briefly, most of the embodiments of the present invention provide a phosphor material that includes a blend of a first phosphor, a second phosphor and a third phosphor. The first phosphor includes a composition having a general formula of $RE_{2-y}M_{1+y}A_{2-y}Sc_ySi_{n-w}Ge_wO_{12+\delta}:Ce^{3+}$, wherein RE is selected from lanthanide ion or Y^{3+}, M is selected from the group consisting of Mg, Ca, Sr, Ba and combinations thereof, A is selected from the group consisting of Mg, Zn and combinations thereof; and $0 \le y \le 2$, $2.5 \le n \le 3.5$, $0 \le w \le 1$, and $-1.5 \le \delta \le 1.5$. The second phosphor includes a complex fluoride doped with manganese (Mn^{4+}), and the third phosphor include a phosphor composition having an emission peak in a range from about 520 nanometers (nm) to about 680 nanometers (nm).

Some embodiments relate to a lighting apparatus. The lighting apparatus includes a light source; and a phosphor material radiationally coupled to the light source. The light source (e.g., light emitting diode (LED)) is capable of emitting radiation in a range from about 400 nanometers to about 480 nanometers. The phosphor material includes a blend of a first phosphor, a second phosphor and a third phosphor. The first phosphor includes a composition having a general formula $RE_{2-y}M_{1+y}A_{2-y}Sc_ySi_{n-w}Ge_wO_{12+\delta}:Ce^{3+}$, wherein RE a is selected from lanthanide ion or Y^{3+}, M is selected from the group consisting of Mg, Ca, Sr, Ba and combinations thereof, A is selected from the group consisting of Mg, Zn and combinations thereof; and $0 \le y \le 2$, $2.5 \le n \le 3.5$, $0 \le w \le 1$, and $-1.5 \le \delta \le 1.5$. The second phosphor includes a complex fluoride doped with manganese (Mn^{4+}), and the third phosphor include a phosphor composition having an emission peak in a range from about 520 nm to about 680 nm.

DRAWINGS

These and other features, aspects, and advantages of the present invention will become better understood when the following detailed description is read with reference to the accompanying drawings in which like characters represent like parts throughout the drawings, wherein:

FIG. **1** is a schematic cross sectional view of a lighting apparatus according to one embodiment of the invention;

FIG. **2** is a schematic cross sectional view of a lighting apparatus according to one embodiment of the invention;

FIG. **3** is a schematic cross sectional view of a lighting apparatus according to one embodiment of the invention;

FIG. **4** is a schematic cross sectional view of a lighting apparatus according to one embodiment of the invention;

FIG. **5** is a schematic cross sectional view of a lighting apparatus according to one embodiment of the invention;

FIG. **6** shows the emission spectra of a phosphor blend using a 450 nm excitation wavelength, in accordance with an exemplary embodiment of the invention;

FIG. 7 shows the emission spectra of a phosphor blend using a 450 nm excitation wavelength, in accordance with another exemplary embodiment of the invention;

DETAILED DESCRIPTION

Approximating language, as used herein throughout the specification and claims, may be applied to modify any quantitative representation that could permissibly vary without resulting in a change in the basic function to which it is related. Accordingly, a value modified by a term or terms, such as "about," is not limited to the precise value specified. In some instances, the approximating language may correspond to the precision of an instrument for measuring the value.

In the following specification and the claims that follow, the singular forms "a", "an" and "the" include plural referents unless the context clearly dictates otherwise.

As used herein, the terms "may" and "may be" indicate a possibility of an occurrence within a set of circumstances; a possession of a specified property, characteristic or function; and/or qualify another verb by expressing one or more of an ability, capability, or possibility associated with the qualified verb. Accordingly, usage of "may" and "may be" indicates that a modified term is apparently appropriate, capable, or suitable for an indicated capacity, function, or usage, while taking into account that in some circumstances the modified term may sometimes not be appropriate, capable, or suitable. For example, in some circumstances, an event or capacity can be expected, while in other circumstances the event or capacity cannot occur—this distinction is captured by the terms "may" and "may be".

The terms "first," "second," and the like, herein do not denote any order, quantity, or importance, but rather are used to distinguish one element from another.

As used herein, the term "phosphor" or "phosphor material" or "phosphor composition" may be used to denote both a single phosphor composition as well as a blend of two or more phosphor compositions. The phosphor blend may contain blue, red, yellow, orange and green phosphors. The blue, red, yellow, orange and green phosphors are so called or known after the color of their light emission.

As used herein, the terms "substitution" and "doping" refer to adding an amount of an element in a material. Typically, an element in a material is partially or fully replaced by another element on such addition. It should be noted that various phosphors described herein may be written down by enclosing different elements in parentheses and separated by commas to show substitution or doping, such as in the case of $((Ba,Ca,Sr)_{1-x}Eu_x)_2Si_5N_8$. As understood by those skilled in the art, this type of notation means that the phosphor can include any or all of those specified elements in the formulation in any ratio. That is, this type of notation for the above phosphor, for example, has the same meaning as $((Ba_aCa_bSr_{1-a-b})_{1-x}Eu_x)_2Si_5N_8$, where a and b can vary from 0 to 1, including the values of 0 and 1.

Particular application is described, herein, in conjunction with converting LED-generated ultraviolet (UV), violet, or blue radiation into white light for general illumination purposes. It should be appreciated, however, that the invention is also applicable to the conversion of radiation from UV, violet and/or blue lasers as well as other light sources to white light.

Embodiments of the present techniques provide phosphor blends that may be used in lighting systems to generate white light suitable for general illumination and other purposes. The phosphor blends include a first phosphor of general formula: $RE_{2-y}M_{1+y}A_{2-y}Sc_ySi_{n-w}Ge_wO_{12+\delta}:Ce^{3+}$, wherein RE is selected from lanthanide ion or Y^{3+}, M is selected from the group consisting of Mg, Ca, Sr, Ba, and combinations thereof, A is selected from the group consisting of Mg, Zn, and combinations thereof; and $0 \le y \le 2$, $2.5 \le n \le 3.5$, $0 \le w \le 1$, and $-1.5 \le \delta \le 1.5$. In one embodiment, the first phosphor may also be represented by general formula of $(RE_{1-x-z}Sc_xCe_z)_2M_{3-p}A_pSi_{n-w}Ge_wO_{12+\delta}$, wherein RE is selected from lanthanide ion or Y^{3+}, M is selected from the group consisting of Mg, Ca, Sr, Ba, and combinations thereof, A is selected from the group consisting of Mg, Zn, and combinations thereof; and $0 \le x \le 1$, $0 \le z \le 0.3$, $0 \le p \le 2$, $2.5 \le n \le 3.5$, $0 \le w \le 1$, and $-1.5 \le \delta \le 1.5$. Advantageously, the phosphors made according to these formulations may maintain high emission intensity (quantum efficiency) across a wide range of temperatures. The phosphors may be used in lighting systems, such as LEDs and fluorescent tubes, among others, to produce blue and blue/green light.

In some embodiments, the first phosphor may have general formula of $(Ca_{1-z}Ce_z)_3Sc_2Si_{n-w}Ge_wO_{12}$, where $0 < z \le 0.3$. Specific embodiments of the first phosphor include the compositions where the Si, Ge component includes at least about 66% Si^{4+}, at least about 83% Si^{4+}, and 100% Si^{4+}. Thus some specific embodiments include $(Ca_{1-z}Ce_z)_3Sc_2(Si_{1-c}Ge_c)_3O_{12}$ where c is from 0.67 to 1.

These phosphors of above formula, have reduced quenching of the luminescence at high temperatures (thermal quenching) as compared to many current phosphors, for example YAG:Ce. Accordingly, these phosphors maintain their emission intensity across a large range of temperatures, which may mitigate losses of intensity or lamp color shifts as the temperature of a lighting system increases during use.

The phosphor blends, further include a second phosphor that is a red line emitter and a third phosphor that has a peak emission in a broad wavelength range from about 520 nm to about 680 nm. The second phosphor may be a complex fluoride that is a line emitter and generates red light. Suitable examples include complex fluorides doped with Mn^{4+}, for example $(Na, K, Rb, Cs, NH_4)_2[(Ti, Ge, Sn, Si, Zr, Hf)F_6]:Mn^{4+}$ and the like. In certain instances, a complex fluoride doped with Mn^{4+} is $K_2[SiF_6]:Mn^{4+}$ ("PFS") used in some illustrative blend examples further below.

The third phosphor may include a phosphor composition having an emission peak in a range from about 520 nanometers (nm) to about 680 nm. The third phosphor is usually a yellow or a yellow-orange phosphor having broad emission range. Non-limiting examples of suitable third phosphors may include a garnet, a nitride, and an oxynitride. Table 1 shows some of such examples. Any combination having two or more members selected from the group consisting of a garnet, a nitride, and an oxynitride may also be used.

In some embodiments, the third phosphor may be a garnet of general formula $(A, Ce)_3M_{5-a}O_{12-3/2a}$, wherein $0 \le a \le 0.5$, A is selected from the group consisting of Y, Gd, Tb, La, Sm, Pr, Lu, and combinations thereof and M is selected from the group consisting of Sc, Al, Ga, and combinations thereof. An example of such garnet is $Y_3Al_5O_{12}:Ce^{3+}$ (YAG). This garnet YAG has an emission peak in a broad wavelength range from about 525 nm to about 645 nm.

In some embodiments, the third phosphor may be a nitride of general formula $(A, Eu)_xSi_yN_z$, wherein $2x+4y=3z$, and A comprises Ba, Ca, Sr, or a combination thereof. The nitride may be further doped with cerium. Some embodiments include $A_2Si_5N_8:Eu^{2+}$, wherein A comprises Ba, Ca, or Sr. In certain instances, the nitride is of formula $((Ba, Ca, Sr)_{1-a-b} Eu_aCe_b)_2Si_5N_8$, where $0\leq a\leq 1$ and $0\leq b\leq 1$. These nitrides emit in broad wavelength range from about 575 nm to about 675 nm.

In some embodiments, the third phosphor may be an oxynitride phosphor of general formula $A_pB_qO_rN_s$: R, where A comprises barium, B comprises silicon, and R comprises europium; and $2<p<6$, $8<q<10$, $0.1<r<6$, $10<s<15$. In these instances, A may further comprises strontium, calcium, magnesium, or a combination thereof; B may further comprise aluminum, gallium, germanium, or a combination thereof; and R may further comprise cerium. In certain instances, the oxynitide phosphor is of formula $(Ba, Ca, Sr, Mg)_4Si_9O_rN_{14.66-(2/3)r}$: Eu such that r is greater than about 1 and less than or equal to about 4. The emission peak of these oxynitrides emit in wavelength range from about 545 nm to about 645 nm.

TABLE 1

Formulas of the third phosphor used in the phosphor blend

Name	Formula
Garnet	$Y_3Al_5O_{12}:Ce^{3+}$
Nitride	$((Ba, Ca, Sr)_{1-a-b}Eu_aCe_b)_2Si_5N_8$, where $0 \leq a \leq 1$ and $0 \leq b \leq 1$
Oxynitride	$(Ba, Ca, Sr, Mg)_4Si_9O_rN_{14.66-(2/3)r}$; where $1 < r < 4$

Each of the general formulas listed herein is independent of every other general formula listed. Specifically, x, y, z, and other variables that may be used as numeric placeholders in a formula are not related to any usage of x, y, z and other variables that may be found in other formulas or compositions.

When the phosphor material includes a blend of two or more phosphors, the ratio of each of the individual phosphors in the phosphor blend may vary, depending on the characteristics of the desired light output, for example color temperature. The relative amounts of each phosphor in the phosphor blend can be described in terms of spectral weight. The spectral weight is the relative amount that each phosphor contributes to the overall emission spectrum of the device. The spectral weight amounts of all the individual phosphors and any residual bleed from the LED source should add up to 100%. In a preferred embodiment, each of the above described phosphors in the blend will have a spectral weight ranging from about 1 percent to about 70 percent.

The relative proportions of each phosphor in the phosphor blends may be adjusted, so that when their emissions are blended and employed in a lighting device, there is produced visible light of predetermined ccx and ccy values on the CIE (International Commission on Illumination) chromaticity diagram. As stated, a white light is preferably produced. This white light may, for instance, possess a ccx value in the range of about 0.25 to about 0.55, and a ccy value in the range of about 0.25 to about 0.55.

The phosphors used to make phosphor blends, may be produced by mixing powders of the constituent compounds and then firing the mixture under a reducing atmosphere. Typically, oxygen-containing compounds of the relevant metals are used. For example, the exemplary phosphor $(Ca_{0.97}Ce_{0.03})_3Sc_2Si_3O_{12}$, discussed further in the examples below, may be produced by mixing the appropriate amounts of oxygen-containing compounds of calcium, cerium, scandium, and silicon, and then firing the mixture under a reducing atmosphere. Silicon may also be provided via silicic acid. After firing, the phosphor may be ball milled, or otherwise ground, to break up any conglomerates that may have formed during the firing procedure. The grinding may be performed after all firing steps are completed, or may be interspersed with additional firing steps.

Non-limiting examples of suitable oxygen-containing compounds include oxides, hydroxides, alkoxides, carbonates, nitrates, silicates, citrates, oxalates, carboxylates, tartarates, stearates, nitrites, peroxides and combinations of these compounds. In embodiments containing carboxylates, the carboxylates used may generally have from one to five carbon atoms, such as formates, ethanoates, proprionates, butyrates, and pentanoates, although carboxylates having larger numbers of carbon atoms may be used. The individual phosphor compositions and a blend of these phosphors may be synthesized by any known method, for example as described in U.S. Pat. No. 7,094,362 B2.

Further, the first phosphors, the second phosphors and the third phosphors discussed above may be blended to form a phosphor blend. For example, phosphor blends may be made that contain the first phosphor having the general formula $(Ca_{0.97}Ce_{0.03})_3Sc_2Si_3O_{12}$, the second phosphor having the general formula $K_2[SiF_6]:Mn^{4+}$, and the third phosphor of general formula $Y_3Al_5O_{12}:Ce^{3+}$ (YAG). An activator ion may be used in these phosphors to obtain the desired emission spectrum. As used herein, the term "activator ion" refers to an ion (for example Ce^{3+}) doped in a phosphor that forms luminescent center and is responsible for the luminescence of the phosphor. Such ions may include ions of Pr, Sm, Eu, Tb, Dy, Tm, Er, Ho, Nd, Bi, Yb, Pb, Yb, Mn, Ag, Cu, or any combinations thereof.

In addition to the synthesis procedures discussed above, many of the phosphors that may be used in the blends described herein may be commercially available. For example, the phosphor YAG, used in blend calculations in presently disclosed phosphor blends, may be commercially available.

The phosphors listed above are not intended to be limiting. Any other phosphors, commercial and non-commercial, that form non-reactive blends with the phosphors of the present techniques may be used in blends and are to be considered to be within the scope of the present techniques. Furthermore, some additional phosphors may be used, e.g., those emitting throughout the visible spectrum region, at wavelengths substantially different from those of the phosphors described herein. These additional phosphors may be used in the blend to customize the white color of the resulting light, and to produce sources with improved light quality. In some embodiments, an additional phosphor may be a phosphor of general formula: $((Sr_{1-z}M_z)_{1-(x+w)}A_wCe_x)_3(Al_{1-y}Si_y)O_{4+y+3(x-w)}F_{1-y-3(x-w)}$; wherein $0<x\leq 0.10$ and $0\leq y\leq 0.5$, $0\leq z\leq 0.5$, $0\leq w\leq x$; A is selected from the group consisting of Li, Na, K, Rb, and a combination thereof; and M is selected from the group consisting of Ca, Ba, Mg, Zn, and a combination thereof.

One embodiment of the invention is directed to a lighting apparatus that includes a phosphor blend radiationally coupled to a light source. As used herein, the term "radiationally coupled" means that the elements are associated with each other so that at least part of the radiation emitted from one is transmitted to the other. A combination of the light from the light source and the light from the phosphor blend may be used to produce white light. For example, a white LED may be based on a blue emitting InGaN chip. The blue emitting chip may be coated with the phosphor blend to convert some of the blue radiation to a complementary color, e.g. a yellow-green emission.

Non-limiting examples of lighting apparatus or devices include devices for excitation by light-emitting diodes (LEDs), fluorescent lamps, cathode ray tubes, plasma display devices, liquid crystal displays (LCD's), UV excitation devices, such as in chromatic lamps, lamps for backlighting liquid crystal systems, plasma screens, xenon excitation lamps, and UV excitation marking systems. These uses are meant to be merely exemplary and not exhaustive.

The light emitted from the lighting apparatus may be characterized using any number of standard measurements. This characterization may normalize the data and make the comparison of light emitted by different lighting apparatus easier to determine. For example, the total of the light from a phosphor and from an LED chip provides a color point with corresponding color coordinates (x and y) in the CIE 1931 chromaticity diagram and correlated color temperature (CCT), and its spectral distribution provides a color rendering capability, measured by the color rendering index (CRI). The CRI is commonly defined as a mean value for 8 standard color samples (R1-8), usually referred to as the general Color Rendering Index, or Ra. A higher value for CRI produces a more "natural" appearance for illuminated objects. By definition, an incandescent light has a CRI of 100, while a typical compact fluorescent light may have a CRI of about 82. Further, the luminosity, or apparent brightness, of a source may also be determined from the spectrum of the emitted light. The luminosity is measured as lumens/W-opt, which represents the number of lumens that 1 watt of light having a particular spectral distribution would represent. A higher lumens/W-opt value indicates that a particular source would appear brighter to an observer.

As the light emitted from combined lighting apparatus components is generally additive, the final spectra of phosphor blends and/or lighting apparatus may be predicted. For example, the amount of light emitted from each phosphor in a blend may be proportional to the amount of that phosphor within the blend. Accordingly, the emission spectrum resulting from the blend can be modeled, and the spectral properties, e.g., the CCT, the CRI, color axes (x and y), and 1 m/W-opt may be calculated from the predicted emission spectrum. Various blends that may be made using the phosphors described above are discussed in the examples below.

Referring to the figures now, FIG. **1** illustrates an exemplary LED based lighting apparatus or lamp **10** that may incorporate the phosphor blends of the present techniques. The LED based lighting apparatus **10** includes a semiconductor UV or visible light source, such as a light emitting diode (LED) chip **12**. Power leads **14** that are electrically attached to the LED chip **12** provide the current that causes the LED chip **12** to emit radiation. The leads **14** may include thin wires supported on thicker package leads **16** or the leads may comprise self-supported electrodes and the package lead may be omitted. The leads **14** provide current to the LED chip **12** and thus cause the LED chip **12** to emit radiation.

The lamp **10** may include any semiconductor blue or UV light source that is capable of producing white light when its emitted radiation is directed onto the phosphor. In one embodiment, the semiconductor light source comprises a blue emitting LED doped with various impurities. Thus, the LED **12** may comprise a semiconductor diode based on any suitable III-V, II-VI or IV-IV semiconductor layers and having an emission wavelength of about 380 to 550 nm. In particular, the LED may contain at least one semiconductor layer comprising GaN, ZnSe or SiC. For example, the LED may comprise a nitride compound semiconductor represented by the formula $In_iGa_jAl_kN$ (where 0≤i; 0≤j; 0≤k and i+j+k=1) having an emission wavelength greater than about 380 nm and less than about 550 nm. Preferably, the chip is a near-UV or blue emitting LED having a peak emission wavelength from about 400 to about 500 nm. Such LED semiconductors are known in the art. The light source as described herein is an LED for convenience. However, as used herein, the term is meant to encompass all semiconductor light sources including, e.g., semiconductor laser diodes.

In addition to inorganic semiconductors, the LED chip **12** may be replaced by an organic light emissive structure or other light sources. Other types of light sources may be used in place of LEDs, such as the gas discharge device discussed with respect to FIG. **5**, below. Examples of gas discharge devices include low-, medium-, and high-pressure mercury gas discharge lamps.

The LED chip **12** may be encapsulated within a shell **18**, which encloses the LED chip and an encapsulant material **20** (also referred to as "encapsulant"). The shell **18** may be glass or plastic. The encapsulant **20** may be an epoxy, plastic, low temperature glass, polymer, thermoplastic, thermoset material, resin, silicone, silicone epoxy, or any other type of LED encapsulating material. Further, the encapsulant **20** may be a spin-on glass or some other high index of refraction material. Typically, the encapsulant material **20** is an epoxy or a polymer material, such as silicone. The shell **18** and the encapsulant **20** are transparent, that is substantially optically transmissive, with respect to the wavelength of light produced by the LED chip **12** and a phosphor material **22**, such as the phosphor blends of the present techniques. However, if the LED chip **12** emits light that is within the UV spectrum, the encapsulant **20** may only be transparent to light from the phosphor material **22**. The LED based lighting apparatus **10** may include an encapsulant **20** without an outer shell **18**. In this application, the LED chip **12** may be supported by the package leads **16**, or by a pedestal (not shown) mounted to the package leads **16**.

The phosphor material **22** is radiationally coupled to the LED chip **12**. In one embodiment, the phosphor material **22** may be deposited on the LED chip **12** by any appropriate method. For example, a solvent based suspension of phosphors can be formed, and applied as a layer onto the surface of the LED chip **12**. In a contemplated embodiment, a silicone slurry in which the phosphor particles are randomly suspended may be placed over the LED chip **12**. Thus, the phosphor material **22** may be coated over or directly on the light emitting surface of the LED chip **12** by coating and drying the phosphor suspension over the LED chip **12**. As the shell **18** and the encapsulant **20** will generally be transparent, an emitted light **24** from the LED chip **12** and the phosphor material **22** will be transmitted through those elements. Although not intended to be limiting, in one embodiment, the median particle size of the phosphor material **22** as measured by light scattering may be from about 1 to about 15 microns.

A second structure that may incorporate the phosphor blends of the present techniques is illustrated in the cross section of FIG. **2**. The structure in FIG. **2** is similar to that of FIG. **1**, except that the phosphor material **22** is interspersed within the encapsulant **20**, instead of being formed directly on the LED chip **12**. The phosphor material **22** may be interspersed within a single region of the encapsulant **20** or throughout the entire volume of the encapsulant **20**. Radiation **26** emitted by the LED chip **12** mixes with the light emitted by the phosphor material **22**, and the mixed light may be visible through the transparent encapsulant **20**, appearing as emitted light **24**.

The encapsulant **20** with the interspersed phosphor material **22** may be formed by any number of suitable plastics processing techniques. For example, the phosphor material **22** may be combined with a polymer precursor, molded around the LED chip **12**, and then cured to form the solid encapsulant **20** with the interspersed phosphor material **22**. In another technique, the phosphor material **22** may be blended into a molten encapsulant **20**, such as a polycarbonate, formed around the LED chip **12**, and allowed to cool. Processing techniques for molding plastics that may be used, such as injection molding, are known in the art.

FIG. **3** illustrates a cross section of a structure that may incorporate the phosphor material **22** of the present techniques. The structure shown in FIG. **3** is similar to that of FIG. **1**, except that the phosphor material **22** may be coated onto a surface of the shell **18**, instead of being formed over the LED chip **12**. Generally, the phosphor material **22** is coated on the inside surface of the shell **18**, although the phosphor material **22** may be coated on the outside surface of the shell **18**, if desired. The phosphor material **22** may be coated on the entire surface of the shell **18** or only a top portion of the surface of the shell **18**. The radiation **26** emitted by the LED chip **12** mixes with the light emitted by the phosphor material **22**, and the mixed light appears as emitted light **24**.

The structures discussed with respect to FIGS. **1-3** may be combined, with the phosphor material located in any two or all three locations or in any other suitable location, such as separately from the shell or integrated into the LED. Further, different phosphor blends may be used in different parts of the structure.

In any of the above structures, the LED based lighting apparatus **10** may also include a plurality of particles (not shown) to scatter or diffuse the emitted light. These scattering particles would generally be embedded in the encapsulant **20**. The scattering particles may include, for example, particles made from Al_2O_3 (alumina) or TiO_2. The scattering particles may effectively scatter the light emitted from the LED chip **12**, and are generally selected to have a negligible amount of absorption.

In addition to the structures above, the LED chip **12** may be mounted in a reflective cup **28**, as illustrated by the cross section shown in FIG. **4**. The reflective cup **28** may be made from or coated with a reflective material, such as alumina, titania, or other dielectric powder known in the art. Generally, the reflective surface may be made from Al_2O_3. The remainder of the structure of the LED based lighting apparatus **10** of FIG. **4** is the same as that of the previous figure, and includes two leads **16**, a conducting wire **30** electrically connecting the LED chip **12** with one of the leads **16**, and an encapsulant **20**. The reflective cup **28** may conduct current to energize the LED chip **12**, or a second conducting wire **32** may be used for the same. The phosphor material **22** may be dispersed throughout the encapsulant **20**, as described above, or may be dispersed in a smaller transparent casing **34** formed within the reflective cup **28**. Generally, the transparent casing **34** may be made from the same materials as the encapsulant **20**. The use of the transparent casing **34** within the encapsulant **20** may be advantageous in that a smaller amount of the phosphor material **22** may be required than if the phosphor were to be dispersed throughout the encapsulant **20**. The encapsulant **20** may contain particles (not shown) of a light scattering material, as previously described to diffuse the emitted light **24**.

FIG. **5** is a perspective view of a lighting apparatus **36** based on a gas discharge device, such as a fluorescent lamp, which may use the phosphor blends of the present techniques. The lamp **36** may include an evacuated sealed housing **38**, an excitation system **42** for generating UV radiation and located within the housing **38**, and a phosphor material **22** disposed within the housing **38**. End caps **40** are attached to either end of the housing **38** to seal the housing **38**.

In a typical fluorescent lamp, the phosphor material **22**, such as the phosphor blends of the present techniques, may be disposed on an inner surface of the housing **38**. The excitation system **42** for generating the UV radiation may include an electron generator **44** for generating high-energy electrons and a fill gas **46** configured to absorb the energy of the high-energy electrons and emit UV light. For example, the fill gas **46** may include mercury vapor, which absorbs energy of the high-energy electrons and emits UV light. In addition to mercury vapor, the fill gas **46** may include a noble gas such as argon, krypton, and the like. The electron generator **44** may be a filament of a metal having a low work function (for example, less than 4.5 eV), such as tungsten, or a filament coated with alkaline earth metal oxides. Pins **48** may be provided to supply electrical power to the electron generator **44**. The filament is coupled to a high-voltage source to generate electrons from the surface thereof.

The phosphor material **22** is radiationally coupled to the UV light from the excitation system **42**. As previously described, radiationally coupled means that the phosphor material **22** is associated with the excitation system **42** so that radiation from the UV light from the excitation system **42** is transmitted to the phosphor material **22**. Thus, a phosphor material that is radiationally coupled to the excitation system **42** may absorb radiation, such as the UV light emitted by the excitation system **42**, and, in response, emit longer wavelengths, such as blue, blue-green, green, yellow, or red light. The longer wavelength of light may be visible as emitted light **24** transmitted through the housing **38**. The housing **38** is generally made of a transparent material such as glass or quartz. Glass is commonly used as the housing **38** in fluorescent lamps, as the transmission spectrum of the glass may block a substantial portion of the "short wave" UV radiation, i.e., light having a wavelength of less than about 300 nm.

A particulate material, such as TiO_2 or Al_2O_3, may be used in conjunction with the phosphor blend **22** to diffuse light generated by the light source **36**. Such a light scattering material may be included with the phosphor blend **22** or separately disposed as a layer between the inner surface of the housing **38** and the phosphor blend **22**. For a fluorescent tube, it may be advantageous to have the median size of the particles of the scattering material range from about 10 nm to about 400 nm.

Although the lighting apparatus or the lamp **36** shown in FIG. **5** has a straight housing **38**, other housing shapes may be used. For example, a compact fluorescent lamp may have a housing **38** that has one or more bends or is in a spiral shape, with electrical supply pins **48** that are disposed at one end of the lamp **36**.

By assigning appropriate spectral weights for each phosphor, one can create spectral blends to cover the relevant portions of color space for white lamps. Specific examples of this are shown below. For various desired CCT's, CRT's and color points, one can determine the appropriate amounts of each phosphor to include in the blend. Thus, one can customize phosphor blends to produce almost any CCT or color point, with corresponding high CRI. Of course, the color of each phosphor will be dependent upon its exact composition (for example relative amounts of Ba, Ca, Sr, as well as Eu in nitride phosphor), which can change the color of the phosphor to a degree where it may have to be renamed. However, determining the changes in the spectral weight to produce the same or similar characteristic lighting device necessitated by such variations is trivial and can be accomplished by one skilled in the art using various methodologies, such as design of experiment (DOE) or other strategies.

By use of the present invention, particularly the blends described in herein, lamps can be provided having high luminosity and general CRI values greater than about 80, for a low range of color temperatures of interest (2500 K to 4000 K) for general illumination. In some blends, the CRI values approach the theoretical maximum of 100. In addition, the R_9 value for these blends can exceed about 90 and approach the theoretical maximum as well. Table 1 and Table 2 show luminosity, CRI values and R_9 values of various blends at CCT values 2700K and 3000K, respectively.

EXAMPLES

The examples that follow are merely illustrative, and should not be construed to be any sort of limitation on the scope of the claimed invention.

TABLE 2

Formulas of example phosphors used in the phosphor blend

Name	Formula
CaSiG	$(Ca_{0.97}Ce_{0.03})_3Sc_2Si_3O_{12}$
PFS	$K_2[SiF_6]:Mn^{4+}$
YAG	$Y_3Al_5O_{12}:Ce^{3+}$
C-BASIN	$Ba_{1.538}Ca_{0.4}Eu_{0.06}Ce_{0.002}Si_5N_8$
YON	$Ba_4Si_9O_4N_{12}:Eu^{2+}$
SASOF	$(Sr_{0.895}Ca_{0.1}Ce_{0.005})_3Al_{0.6}Si_{0.4}O_{4.4}F_{0.6}$

TABLE 3

Examples of phosphor blend produced

Example.	Phosphor blend
Example 1	CaSiG/YAG/PFS
Example 2	CaSiG/YON/PFS
Example 3	CaSiG/CBASIN/PFS
Example 4	CaSiG/SASOF/PFS/YAG

TABLE 4

S. No.	CCT	Wavelength of LED emission (nm)	Spectral weight of LED emission	Spectral weight of YAG	Spectral weight of PFS	Spectral weight of YON	Spectral weight of CaSiG	Spectral weight of CBASIN	Spectral weight of SASOF	Lumenosity (lumen/watt)	CRI	R9
1	2700K	430	0.099	0.499	0.295		0.106			320	85.9	90.7
2		440	0.0805	0.527	0.297		0.0945			328	87.6	92.4
3		450	0.0777	0.552	0.294		0.0753			330	90.1	93.6
4		440	0.0714		0.308	0.25	0.37			328	94.2	94.8
5		450	0.0899		0.273	0.232	0.404			330	95.8	96.9
6		430	0.099	0.461	0.294		0.094		0.05	320	85.9	90.9
7		440	0.0805	0.49	0.297		0.826		0.049	328	87.6	92.5
8	3000K	440	0.0921		0.278	0.2137	0.416			328	92.7	97.7
9		430	0.122	0.442	0.265		0.169			319	85.1	87.7
10		440	0.099	0.475	0.267		0.157			328	87.1	89.7
11		450	0.099	0.508	0.262		0.129			330	90.1	91.1
12		430	0.1		0.04		0.34	0.58		278	94	93
13		440	0.08		0.04		0.34	0.54		283	96	94
14		450	0.07		0.03		0.34	0.56		284	98	93

Various phosphor compositions according to the formulations listed in Table 2, were manufactured. The emission spectra of individual phosphors were obtained, and used in calculations to predict emission spectra for various blends presented in Table 3. Further, the calculations also included any visible light emitted by a light source. FIGS. **6** and **7** show the predicted emission spectra of the examples 1 and 2 of the blends in Table 3. The predicted amount of each phosphor based on spectral weight is shown in the Table 4 along with the spectral contribution of the emissions from the light sources, for example blue LEDs having peak wavelengths of 430 nm, 440 nm and 450 nm. Further, the spectral characteristics calculated from the predicted spectra for these blends are also presented in Table 4. FIGS. **6** and **7** correspond to the blend examples No. 4 and 3, respectively, of Table 4. Advantageously, these blends generate white light having high luminosity, a high CRI value and a low CCT that can be tuned between 2500K and 3000K.

While only certain features of the invention have been illustrated and described herein, many modifications and changes will occur to those skilled in the art. It is, therefore, to be understood that the appended claims are intended to cover all such modifications and changes as fall within the true spirit of the invention.

The invention claimed is:

1. A phosphor material comprising a blend of:

a first phosphor,

wherein the first phosphor comprises a composition of general formula $(Ca_{1-z}Ce_z)_3Sc_2Si_{n-w}Ge_wO_{12}$, where $0<z\leq0.3$ and $0\leq w\leq1$, and $2.5\leq n\leq3.5$

a second phosphor comprising a complex fluoride doped with manganese (Mn^{4+}), and

a third phosphor comprising a phosphor composition having an emission peak in a range from about 520 nm to about 680 nm, wherein the third phosphor comprises a garnet of formula $Y_3Al_5O_{12}:Ce^{3+}$;

wherein when the phosphor material is radiationally coupled to a light source emitting radiation in a range from about 400 nanometers to about 480 nanometers, results in a white light having CCT of from 2500 K to 4000 K, and R_9 exceeding about 90.

2. The phosphor material of claim **1**, wherein the second phosphor comprises a general formula $A_2[MF_6]:Mn^{4+}$, wherein A is selected from the group consisting of Na, K, Rb, Cs, NH_4, and a combination thereof; and M is selected from the group consisting of Si, Ti, Zr, Mn, and a combination thereof.

3. A phosphor material comprising a blend of:

a first phosphor comprising a composition having a general formula of $RE_{2-y}M_{1+y}A_{2-y}Sc_ySi_{n-w}Ge_wO_{12+\delta}:Ce^{3+}$, wherein RE is selected from lanthanide ion or Y^{3+}, M is selected from the group consisting of Mg, Ca, Sr, Ba, and combinations thereof, A is selected from the group consisting of Mg, Zn, and combinations thereof; and $0 \le y \le 2$, $2.5 \le n \le 3.5$, $0 \le w \le 1$, and $-1.5 \le \delta \le 1.5$,

a second phosphor comprising a complex fluoride doped with manganese (Mn^{4+}), and

a third phosphor comprising a phosphor composition having an emission peak in a range from about 520 nm to about 680 nm, wherein the third phosphor comprises an oxynitride of a general formula $A_pB_qO_rN_s$: R, where A is barium, B is silicon, and R is europium; and $2<p<6$, $8<q<10$, $0.1<r<6$, $10<s<15$.

4. The phosphor material of claim **3**, wherein the second phosphor comprises a general formula $A_2[MF_6]:Mn^{4+}$, wherein A is selected from the group consisting of Na, K, Rb, Cs, NH_4, and a combination thereof; and M is selected from the group consisting of Si, Ti, Zr, Mn, and a combination thereof.

5. A phosphor material comprising a blend of:

a first phosphor comprising a composition having a general formula of $RE_{2-y}M_{1+y}A_{2-y}Sc_ySi_{n-w}Ge_wO_{12+\delta}:Ce^{3+}$, wherein RE is selected from lanthanide ion or Y^{3+}, M is selected from the group consisting of Mg, Ca, Sr, Ba, and combinations thereof, A is selected from the group consisting of Mg, Zn, and combinations thereof; and $0 \le y \le 2$, $2.5 \le n \le 3.5$, $0 \le w \le 1$, and $-1.5 \le \delta \le 1.5$,

a second phosphor comprising a complex fluoride doped with manganese (Mn^{4+}), and

a third phosphor comprising a phosphor composition having an emission peak in a range from about 520 nm to about 680 nm, wherein the third phosphor comprises $A_2Si_5N_8:Eu^{2+},Ce^{3+}$ wherein A is selected from the group consisting of Ba, Ca, Sr, and a combination thereof.

6. The phosphor material of claim **5**, wherein the second phosphor comprises a general formula $A_2[MF_6]:Mn^{4+}$, wherein A is selected from the group consisting of Na, K, Rb, Cs, NH_4, and a combination thereof; and M is selected from the group consisting of Si, Ti, Zr, Mn, and a combination thereof.

7. A lighting apparatus comprising: a light source capable of emitting radiation in a range from about 400 nanometers to about 480 nanometers; and the phosphor material of claim **1** radiationally coupled to the light source.

8. The lighting apparatus of claim **7**, wherein the light source comprises a light emitting diode (LED).

* * * * *